

Water on Silicene: Hydrogen Bond Autocatalysis Induced Physisorption-Chemisorption-Dissociation Transition

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(Dated: March 15, 2016)

ABSTRACT: A single water molecule has nothing special. However, macroscopic water displays many anomalous properties at the interface, such as a high surface tension, hydrophobicity and hydrophilicity. Although the underlying mechanism is still elusive, hydrogen bond is expected to have played an important role. An interesting question is if the few-water molecule clusters will be qualitatively different from a single molecule. Using adsorption behavior as an example, by carefully choosing two-dimensional silicene as the substrate material, we demonstrate that water monomer, dimer and trimer show contrasting properties. The additional water molecules in dimer and trimer induce a transition from physisorption to chemisorption then to dissociation on silicene. Such a hydrogen bond autocatalytic effect is expected to have a broad application potential in silicene-based water molecule sensor and metal-free catalyst for water dissociation.

KEYWORDS: Water adsorption, hydrogen bond, silicene, physisorption, chemisorption, dissociation and density functional theory

INTRODUCTION

Hydrogen bonding is crucial in many molecular and supramolecular systems, such as water, polymers and proteins. It determines many of their chemical and physical properties.[1–3] Hydrogen bonding in water plays an important role in distinguishing it from other systems with comparable molecular mass. At the same time, water is also unique among other hydrogen-bonded systems since it has a very large number of hydrogen bonds per unit mass. Beyond bulk properties, the structure of water at the interface with other materials can induce many anomalous properties, such as a high surface tension of water, hydrophobicity and hydrophilicity.[4] In fact, water at the interface plays a critical role in wide aspects ranging from daily life to science and technology.

In recent years, two-dimensional (2D) ultrathin materials,[5–8] such as graphene,[9–11] silicene,[12–15] germanene,[16–18] phosphorene,[19–21] hexagonal boron nitride (h-BN),[22–24] and molybdenum disulphide (MoS₂),[25–27] have received considerable interest owing to their remarkable properties and wide applications. In particular, graphene,[9–11] a 2D sp²-hybridized carbon sheet, is known to have remarkable electronic properties, such as a high carrier mobility. The water-graphene interface also been widely studied experimentally[28–32] and theoretically,[33–38] for the purpose to realize charge doping,[31] charge transfer[34] and band-gap opening[35] for graphene based field effect transistors, molecule sensor,[28] metal-free catalyst for oxygen reduction reaction[30] and water dissociation.[33] 2D low-cost graphene has more large contact area for

water adsorption than traditional 3D noble metals and metal oxides,[4] such as platinum[39–41] and TiO₂,[42–44] as the catalysts for water chemisorption and dissociation. However, water molecules are physically adsorbed on graphene with very small adsorption energies via weak van der Waals interactions[35] and graphene is strongly hydrophobic,[36] preventing immediate practical applications on graphene based sensitive molecule sensor and efficient catalyst if without introducing dopants or defects.[30, 32, 33, 37]

Silicene, analog to graphene but with buckled honeycomb structures,[12–14] has also attracted increasing attentions for its excellent properties[15] similar to graphene, such as high carrier mobility,[45] electric response,[46] ferromagnetism,[47] quantum Hall effect,[48] giant magnetoresistance[49] and superconductivity.[50] Silicene has been widely experimentally fabricated on Ag[51–54] and Ir[55] substrates. Due to its buckled honeycomb structures, silicene exhibits a much higher chemical reactivity than graphene, showing much stronger adsorption of atoms[56–62] and molecules[63–67] than graphene, with great potential applications on new silicene based nanoelectronic devices,[15] Li-ion storage batteries,[59] hydrogen storage,[60] catalyst,[61] thin-film solar cell absorbers,[62] hydrogen[64] and helium[65] separation membrane, molecule sensor and detection,[66, 67] superior to graphene. However, water monomer is still proved to be physically adsorbed on silicene via van der Waals interactions,[63, 64] similar to graphene.[34–36]

In the present work, by using the first-principles density functional theory calculations and ab-initio molecu-

lar dynamics simulations, we find that hydrogen bonding in water dimer and trimer can induce autocatalytic chemisorption and dissociation of water molecules on silicene. Furthermore, the interaction between water molecules and silicene increases as the number of hydrogen bonding in water molecules. We also find that silicene is hydrophilic different from graphene.

THEORETICAL MODELS AND METHODS

The lattice parameter of silicene calculated to setup unit cell is 3.866 Å, agreeing well with previous theoretical works.[47] In order to simulate the infinite planar monolayer, a 4×4 supercell of silicene containing 32 silicon atoms is adopted. Different adsorption sites (valley, bridge, hollow and top) of water molecules on silicene are considered as shown in Figure 1. The vacuum space in the Z direction is about 20 Å to separate the interactions between neighboring slabs.

We use the first-principles density functional theory (DFT) calculations implemented in the VASP package.[68] We choose the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)[69] as the exchange-correlation functional, and adopt the semi-empirical van der Waals dispersion correction proposed by Grimme (DFT-D2)[70] to describe the weak van der Waals interactions of layered 2D materials and molecular adsorption on surfaces.[71–78] We check the adsorption structures of water molecules on silicone with non-empirical van der Waals density functional (vdW-DF) scheme proposed by Dion et al.[79] and obtain similar results. Because the GGA-PBE method tends to underestimate the bandgap of semiconductors, the screened hybrid HSE06 functional[80] is also used to compute the electronic band structures. We set the energy cutoff to be 500 eV. The surface Brillouin zone is sampled with a 3×3 regular mesh and 120 (GGA-PBE) or 60 (HSE06) k points are used for calculating the small band gaps at the Dirac points of silicene. All the geometry structures are fully relaxed by using the conjugate gradient (CG) algorithm until total energy and atomic forces are converged to 10^{-5} eV and 0.01 eV/Å, respectively. Charge transfer is obtained based on Bader analysis.[81] Ab-initio molecular dynamics (AIMD) simulations are performed in a canonical ensemble with a 4×4 supercell of silicene containing 32 silicon atoms and four layers of water molecules containing 144 oxygen atoms and 288 hydrogen atoms (1.0 g/cm^3). The energy cutoff is set to be 350 eV. The simulations are performed for about 13.0 ps with a time step of 1.0 fs at the temperature of 300 K controlled by a Nose-Hoover thermostat.[82, 83]

In order to evaluate the stability of water molecules on silicene, the adsorption energy is defined as $E_a = E((\text{H}_2\text{O})_n/\text{Silicene}) - E((\text{H}_2\text{O})_n) - E(\text{Silicene})$, where, $E((\text{H}_2\text{O})_n/\text{Silicene})$, $E((\text{H}_2\text{O})_n)$ and $E(\text{Silicene})$ repre-

TABLE I: Adsorption properties of water molecules adsorption on silicene, including adsorption type (Phys/Chem/Diss), adsorption energy E_a (eV), adsorption distance (or Si-O bond length) d (Å), electron transfer from silicene to water molecules ρ (e) and band gap E_g (meV) opened at the Dirac point for water molecules on silicene.

H ₂ O/Silicene	Phase	E_a	d	ρ	E_g
(H ₂ O) ₁ /Silicene (Valley)	Phys	-0.13	2.87	0.21	11
(H ₂ O) ₁ /Silicene (Bridge)	Phys	-0.15	2.92	0.14	23
(H ₂ O) ₁ /Silicene (Hollow)	Phys	-0.16	2.89	0.23	13
(H ₂ O) ₁ /Silicene (Top)	Phys	-0.17	2.49	0.08	66
(H ₂ O) ₂ /Silicene (Top)	Chem	-0.67	1.93	0.23	121
(H ₂ O) ₃ /Silicene (Top)	Chem	-1.19	1.81	0.44	128
(H ₂ O) ₃ /Silicene (Top)	Diss	-1.09	1.77	0.50	152
(H ₂ O) ₁ /Silicene/Ag (Top)	Phys	-0.28	2.33	0.21	-
(H ₂ O) ₂ /Silicene/Ag (Top)	Chem	-0.93	1.90	0.51	-
(H ₂ O) ₃ /Silicene/Ag (Top)	Chem	-1.64	1.79	0.85	-
(H ₂ O) ₃ /Silicene/Ag (Top)	Diss	-1.58	1.75	0.73	-

sent the total energy of water molecules adsorption on silicene, water molecule clusters and pristine silicene, respectively. For water molecule clusters ($n = 2$ and 3), the binding energy of hydrogen bond is defined as $E_b = E((\text{H}_2\text{O})_n) - nE(\text{H}_2\text{O})$, where, $E((\text{H}_2\text{O})_n)$ and $E(\text{H}_2\text{O})$ represent the total energy of water molecule clusters and single water molecule, respectively. As an benchmark, DFT-D2 calculations give a good bilayer distance of 3.25 Å and binding energy of -25 meV per carbon atom for bilayer graphene, fully agreeing with previous experimental[84, 85] and theoretical[86, 87] studies. Furthermore, DFT-D2 calculations also give accurate binding energy of -0.26 eV in water molecule dimer.[88]

RESULTS AND DISCUSSION

We first check the adsorption of water monomer on silicene. Geometric and electronic structures for different adsorption sites are shown in Figure 1 and the corresponding adsorption properties are listed in Table 1. Water monomer is physically adsorbed on silicene via van der Waals interactions,[63, 64] with small adsorption energies (-0.13 ~ -0.17 eV) and large adsorption distances (2.49 ~ 2.92 Å). The top site is the most stable adsorption site. Water adsorption on silicene acts as an electron acceptor (0.08 ~ 0.23 e), similar to graphene.[34–36]

Silicene's linear Dirac-like dispersion relation $E(k) = \pm \hbar \nu_F |k|$ around the Fermi level is slightly affected by adsorption of water monomer. The Fermi velocity $\nu_F = (1/\hbar)(\partial E/\partial k)$ is about 10^5 m/s for water adsorbed silicene, only slightly lower than that of the freestanding silicene. Therefore, silicene's high carrier mobility can

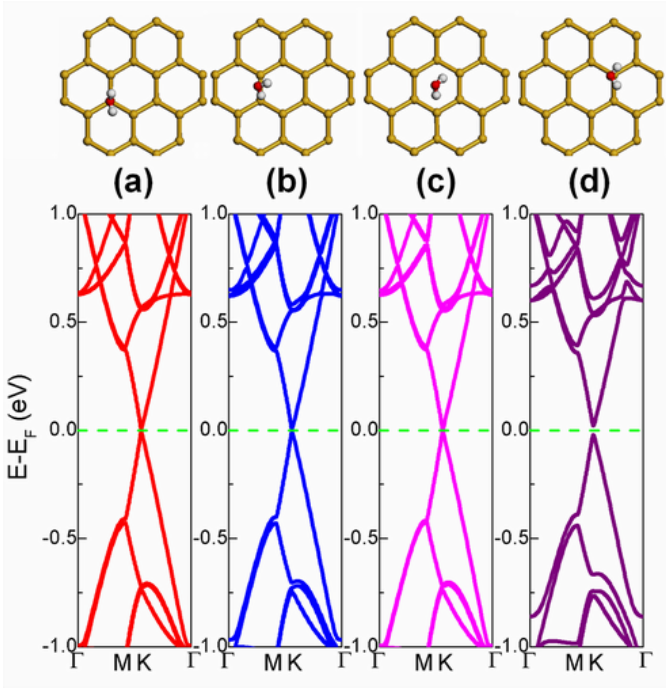


FIG. 1: (Color online) Geometric and electronic structures (HSE06) of water monomer physisorbed on silicene. Different adsorption sites are considered, (a) valley, (b) bridge, (c) hollow and (d) top. The yellow, red and white balls denote silicon, oxygen and hydrogen atoms, respectively. The Fermi level is set to zero and marked by green dotted lines.

be preserved for water molecules adsorption. Upon water molecule adsorption, a small band gap is opened at the Dirac point of silicene. For adsorption at the valley, bridge, and hollow sites, the energy gap is 11, 23 and 13 meV, respectively. They are significantly smaller than thermal fluctuation (about 25 meV) at room temperature, similar to the graphene case. A wider band gap of 66 meV is opened at the Dirac point if water monomer is adsorbed at the top site.

As shown in Figure 2, interestingly, water molecule dimer and trimer are chemically adsorbed and even dissociated on silicene with large adsorption energies (-0.67, -1.19 and -1.09 eV) via strong covalent Si-O bonds (1.93, 1.81 and 1.77 Å) between an oxygen atom (O_a) in water and a top silicon atom. Notice that the adsorption energies predicted here are much larger than the binding energy of hydrogen bond formation in water clusters (only -0.26 eV per hydrogen bond). Therefore, this result suggests that silicene is hydrophilic in contrast to graphene.[36]

Compared to single molecule case, more sizable band gaps (121, 128 and 152 meV) are opened at the Dirac point of silicene for water dimer and trimer chemisorption on silicene and water trimer dissociation on silicene, which are significantly larger than thermal fluctuation

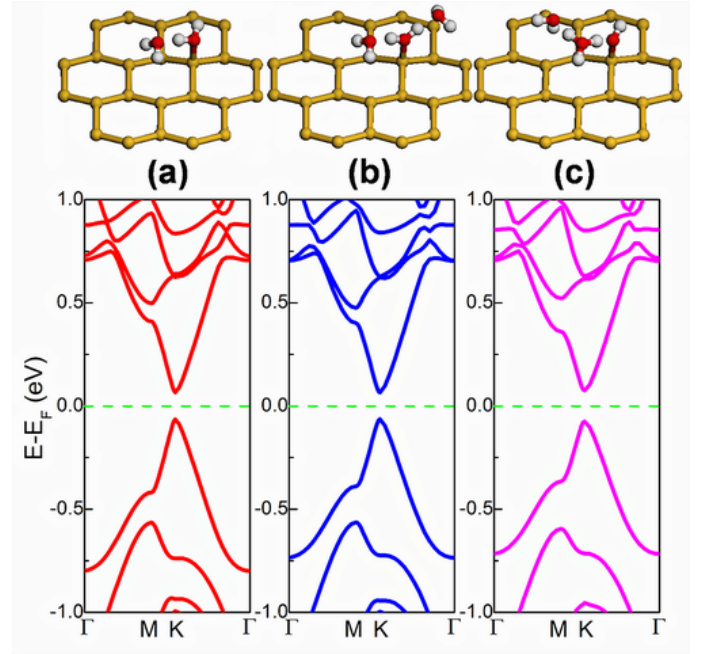


FIG. 2: (Color online) Geometric and electronic structures (HSE06) of water dimer and trimer adsorption on silicene, including the chemisorption of (a) $(H_2O)_2$ /Silicene and (b) $(H_2O)_3$ /Silicene, and (c) the dissociation of $(H_2O)_3$ /Silicene. The yellow, red and white balls denote silicon, oxygen and hydrogen atoms, respectively. The Fermi level is set to zero and marked by green dotted lines.

(25 meV) at room temperature. Furthermore, these gap values also depend sensitively on the adsorbate concentration. Therefore, water cluster adsorbed silicene systems have sizable and tunable band gaps with potential application on silicene based water molecule sensor and field-effect transistors.

Figure 3 shows the differential charge density of water molecules adsorption on silicene ($\Delta\rho = \rho((H_2O)_n/\text{Silicene}) - \rho((H_2O)_n) - \rho(\text{Silicene})$) and the corresponding XY-averaged differential charge density. We find that more electrons (0.23, 0.44 and 0.50 e) transfer from silicene to water in dimer and trimer adsorption, and trimer dissociation, compared to that (0.08 e) in the single water molecule case. Therefore, the interaction between water molecules and silicene increases as the number of hydrogen bonds formation in water molecules increases.

Figure 4 shows total density of states (DOS) of water molecules ($(H_2O)_1$, $(H_2O)_2$ and $(H_2O)_3$) and the corresponding partial density of states (PDOS) of the oxygen atom (O_a) which binds to silicene upon adsorption. The frontier orbitals $1b_1$ (highest occupied molecular orbital (HOMO)) and lowest unoccupied molecular orbital $4a_1$ (LUMO)) of H_2O are far away from the Dirac point of graphene and silicene.[66] Thus, water monomer has

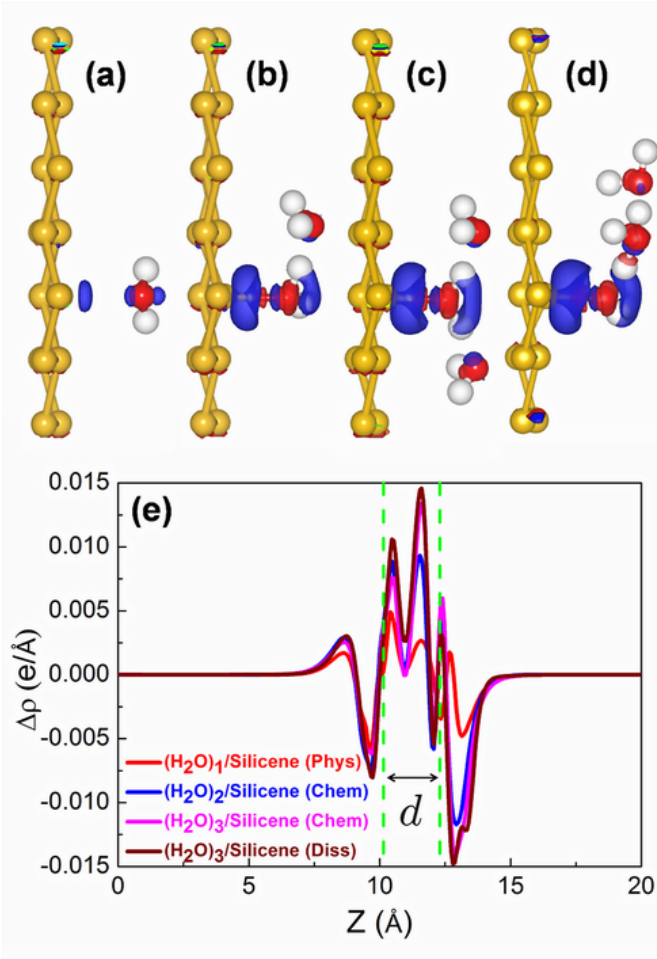


FIG. 3: (Color online) Differential charge density of water molecules adsorption on silicene ($0.04 \text{ e}/\text{\AA}^3$), (a) physisorption of $(\text{H}_2\text{O})_1/\text{Silicene}$, (b) chemisorption of $(\text{H}_2\text{O})_2/\text{Silicene}$, (c) chemisorption of $(\text{H}_2\text{O})_3/\text{Silicene}$ and (d) dissociation of $(\text{H}_2\text{O})_3/\text{Silicene}$. Red (positive) and blue (negative) regions indicate electron increase and decrease, respectively. (e) XY-averaged differential charge density. The water-silicene interface is marked by green dotted lines.

low reactivity to both graphene and silicene. But for water dimer and trimer, the LUMO gets lower and becomes closer to the Fermi level as more hydrogen bonds are formed in water clusters (7.5, 6.6, 6.3 and 6.3 eV respectively for water monomer physisorption, water dimer chemisorption, trimer chemisorption and dissociation on silicene). Especially for the LUMO states contributed by the O_a atom, we find significant energy shift of LUMO in water molecules makes electron transfer from silicene to water easier. Notice that the O_a atom in the structure of water trimer for dissociation on silicene shows more localized LUMO states compared to that in water trimer for chemisorption on silicene. Therefore, the activated O_a atom can form a Si-O bond upon adsorption, showing an autocatalytic behavior for chemisorption and dis-

sociation compared to single water molecule adsorption. Hydrogen bonding in water thus plays an important role in its adsorption at the $\text{H}_2\text{O}/\text{Silicene}$ interface.

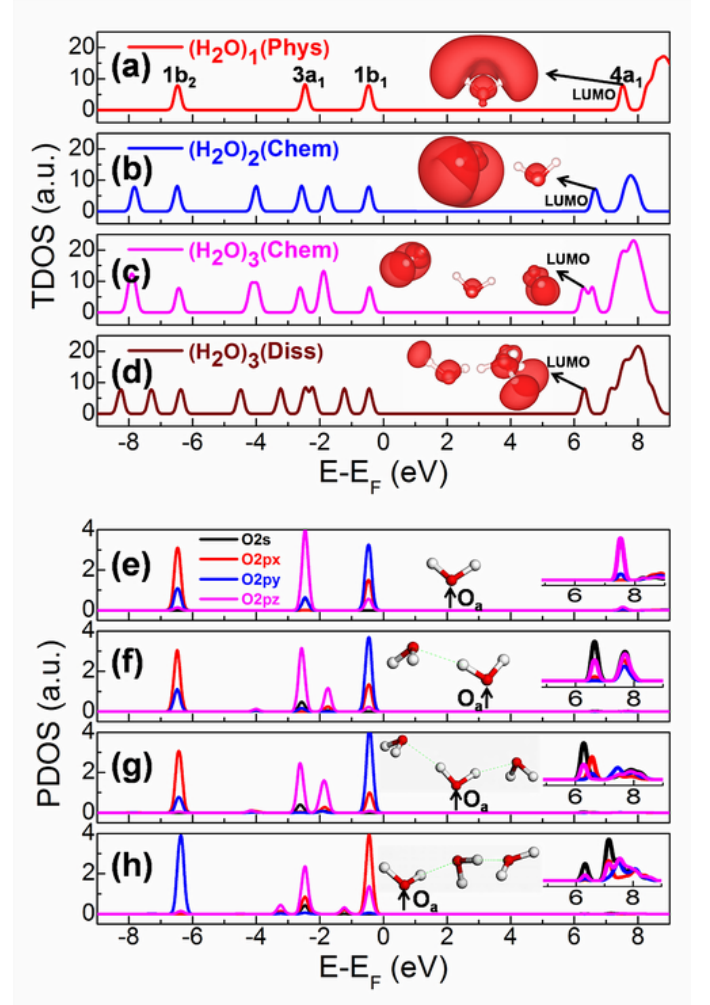


FIG. 4: (Color online) Electronic structures (HSE06) of water clusters ($(\text{H}_2\text{O})_1$, $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$). Total density of states (TDOS) of water molecules, (a) $(\text{H}_2\text{O})_1(\text{Phys})$, (b) $(\text{H}_2\text{O})_2(\text{Chem})$, (c) $(\text{H}_2\text{O})_3(\text{Chem})$ and (d) $(\text{H}_2\text{O})_3(\text{Diss})$. LUMO states of water molecules are shown in the inset. Partial density of states (PDOS) of the adsorption oxygen atom (O_a) of water molecules at the top of silicene, (e) $(\text{H}_2\text{O})_1(\text{Phys})$, (f) $(\text{H}_2\text{O})_2(\text{Chem})$, (g) $(\text{H}_2\text{O})_3(\text{Chem})$ and (h) $(\text{H}_2\text{O})_3(\text{Diss})$. Magnified LUMO is shown in the inset. The Fermi levels of water molecules are set to zero.

We notice that water cluster is physically adsorbed on graphene, which can be understood from the electronic structure difference between graphene and silicene.[64] Although they have similar work functions, the reactive p_z state is closer to the Fermi level in silicene compared to the graphene case. We also check other elemental 2D materials with higher chemical reactivity than graphene, such as germanene and phosphorene. Though oxygen molecules are easily chemically adsorbed and dissociated

on silicene,[63] germanene[89] and phosphorene[90] at room temperature, we find that water molecules are only chemically adsorbed and dissociated on silicene. Therefore, silicene should be a special 2D substrate material for adsorbing water molecules.

To date, it is still a challenge to obtain freestanding silicene. To confirm that the novel adsorption behavior is universal, we also consider silicene on a typical substrate, the Ag(111) surface.[51–54] A 3×3 silicene supercell is used to match a 4×4 supercell of the Ag(111) surface, which gives a negligible lattice mismatch (2%).[52] As shown in Figure 5, water monomer ($d_{Si-O} = 2.33 \text{ \AA}$ and $E_a = -0.28 \text{ eV}$), and water dimer ($d_{Si-O} = 1.90 \text{ \AA}$ and $E_a = -0.93 \text{ eV}$) and trimer ($d_{Si-O} = 1.79 \text{ \AA}$ and $E_a = -1.64 \text{ eV}$) are chemisorbed on Ag-supported silicene. Furthermore, more electrons (0.21, 0.51, 0.85 and 0.73 e) transfer from Ag-supported silicene to water compared to that (0.08, 0.23, 0.44 and 0.50 e) of water molecules adsorbed on free-standing silicene. Therefore, the interaction between water molecules and silicene is strengthened when an Ag substrate is presented, similar to water molecules adsorption on metal-supported grapheme.[38] Although the substrates do have an effect on water adsorption, the autocatalytic behavior we observed is quite robust.

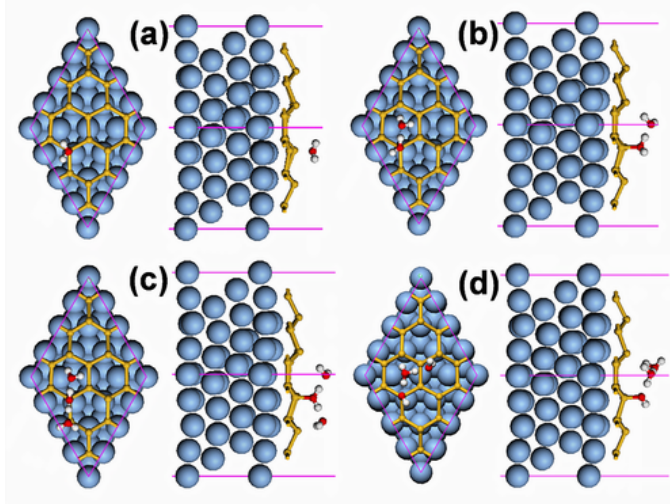


FIG. 5: (Color online) Geometric structures of water molecules adsorption on silicene supported by the Ag(111) surface, including (a) physisorption of $(H_2O)_1/Silicene/Ag$, (b) chemisorption of $(H_2O)_2/Silicene/Ag$, (c) chemisorption of $(H_2O)_3/Silicene/Ag$ and (d) dissociation of $(H_2O)_3/Silicene/Ag$. The yellow, red, white and blue balls denote silicon, oxygen, hydrogen and silver atoms, respectively.

To further confirm the physical picture obtained, AIMD simulations are also performed at room temperature (300 K). As shown in Figure 6, in the initial configuration ($t = 0.0 \text{ ps}$), water molecules are set to be

physically adsorbed on silicene. At $t = 0.3 \text{ ps}$, we find that one water molecule is chemically adsorbed on silicene. At $t = 0.5 \text{ ps}$, more water molecules are chemically adsorbed and some of them are even dissociated on silicene at room temperature. At $t = 1.0 \text{ ps}$, most of water molecules are dissociated on silicene. After $t = 10.0 \text{ ps}$, more and more water molecules are chemically adsorbed and dissociated on silicene at room temperature. Therefore, the chemisorption of water molecules on silicene and the hydrophobicity of silicene provide potential applications on silicene based water molecule sensor and metal-free catalyst for oxygen reduction reaction and water dissociation without introducing dopants or defects.[30, 32, 33, 37]

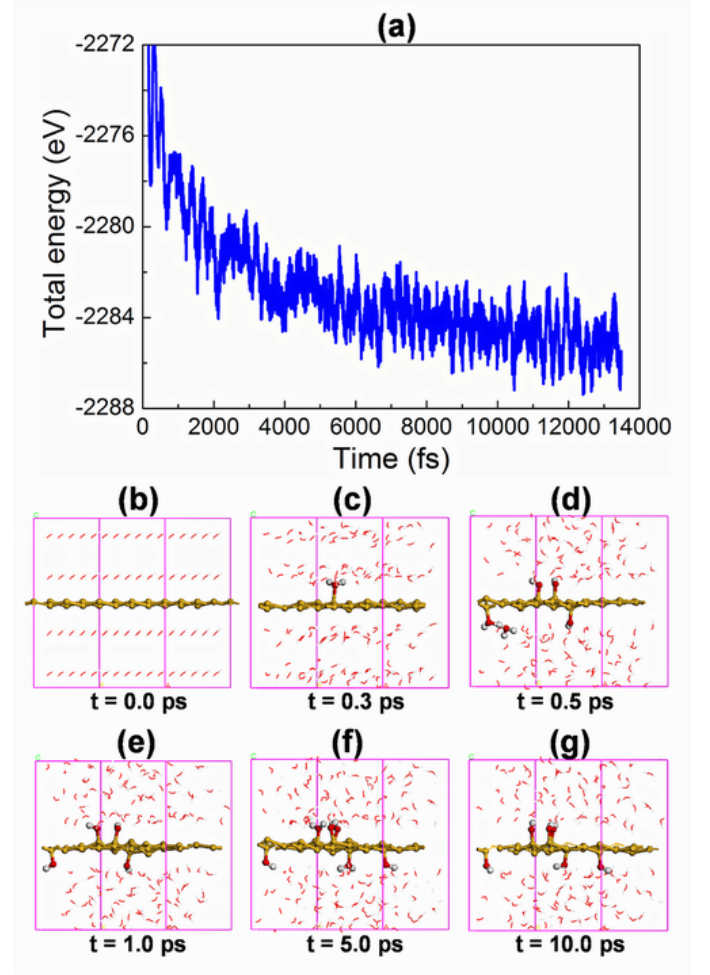


FIG. 6: (Color online) AIMD simulations of water molecules adsorption on silicene. (a) AIMD fluctuations of total energy during 13.0 ps at 300 K. Six snapshots of water molecules adsorption on silicene are shown in the inset, (b) $t = 0.0 \text{ ps}$, (c) $t = 0.3 \text{ ps}$, (d) $t = 0.5 \text{ ps}$, (e) $t = 1.0 \text{ ps}$, (f) $t = 5.0 \text{ ps}$ and (g) $t = 10.0 \text{ ps}$. Water molecules chemically adsorbed and dissociated on silicene are highlighted in the insert.

SUMMARY AND CONCLUSIONS

In summary, we have explored the interaction between water molecules and silicene via density functional theory calculations and ab-initio molecular dynamics simulations. We find that water monomer interacts weakly with silicene via a van der Waals interaction. But, due to the hydrogen bond induced charge transfer, water clusters (dimer and trimer) are chemically adsorbed and dissociated on silicene via strong covalent Si-O bonds. Charge transfer occurs from silicene to water molecules. Our calculations show that silicene is hydrophilic different from other widely studied two-dimensional materials, and the chemisorption and dissociation of water molecule clusters on silicene have immediate applications as water molecule sensor and metal-free catalyst for oxygen reduction reaction and water dissociation without introducing dopants or defects, superior to graphene.

ACKNOWLEDGMENTS

This work is partially supported by the National Key Basic Research Program (2011CB921404), by NSFC (11404109, 21121003, 91021004, 21233007, 21222304), by CAS (XDB01020300). This work is also partially supported by the Scientific Discovery through Advanced Computing (SciDAC) Program funded by U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Sciences (W. H.). We thank the National Energy Research Scientific Computing (NERSC) center, and the USTCSCC, SC-CAS, Tianjin, and Shanghai Supercomputer Centers for the computational resources.

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